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We have performed extensive tight binding calculations of electronic states in HgTe-CdTe heterojunctions, quantum wells and superlattices. The method of solution is based on the Green's function and a powerful renormalization technique, which is particularly suited for the determination of the electronic wavefunctions. That allows a conclusive identification and analysis of the peculiar interface states that occur in these microstructures, and shows the crucial role played by the s-p mixing. In particular, the critical concentration at which the semimetal-semiconductor transition occurs in the simple alloy turns out to be related to a critical concentration occurring in superlattice alloys, at which interfacial states anti-cross, with maximum s-p mixing. We have also applied a new modified (two- or n-step) Lanczos method to determine real and imaginary parts of all the components of the wavefunction amplitude, to confirm or further investigate the complete nodal structure. Furthermore, we have used our results to investigate the question of large vs. small valence band offset for this type of interface. On a separate line of research, we have investigated the linear and nonlinear electrical response of composite systems.



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# Theoretical Study of Alloys and Superlattices with the Renormalization and Recursion Methods

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## I. STATEMENT OF THE PROBLEM STUDIED

We have performed extensive tight binding calculations of electronic states in HgTe-CdTe heterojunctions, quantum wells and superlattices. The method of solution is based on the Green's function and a powerful renormalization technique, which is particularly suited for the determination of the electronic wavefunctions. That allows a conclusive identification and analysis of the peculiar interface states that occur in these microstructures, and shows the crucial role played by the $s-p$ mixing that derives from coupling of $\Gamma_8$- and $\Gamma_6$-like bands of the composing materials. In particular, the critical concentration $x_a$ at which the semimetal-semiconductor transition occurs in the $Hg_{1-x}Cd_xTe$ simple alloy turns out to be related to a critical concentration $x_c$ occurring in $(HgTe)_m(Hg_{1-x}Cd_xTe)_n$ superlattice alloys, at which interfacial states anti-cross, with maximum $s-p$ mixing. We have also applied a new modified (two- or $n-$step) Lanczos method to determine real and imaginary parts of all the components of the wavefunction *amplitude*, to confirm or further investigate the complete nodal structure. Furthermore, we have used our results to investigate the question of large vs. small valence band offset for this type of interface.

On a separate line of research, we have investigated the linear and nonlinear electrical response of composite systems, and obtained a wealth of significant results, which we also summarize in this report.

## II. SUMMARY OF THE MOST IMPORTANT RESULTS FOR THE ELECTRONIC STATES OF HGTE-CDTE MICROSTRUCTURES

A considerable effort to understand the peculiar behavior of HgTe-CdTe quantum wells and superlattices has produced in the last two decades a great deal of good results. Experimental investigations have included most noticeably absorption, photoluminescence, magneto-optical and magneto-transport measurements. Theoretical studies have been based on the effective mass approximation and $\mathbf{k}\cdot\mathbf{p}$ methods, as well as tight-binding (TB)

schemes. This has allowed a fairly consistent interpretation and understanding of a broad range of properties of these microstructures.

Various optoelectronic applications may require further knowledge of accurate wavefunctions: the primary purpose of our work has been that of advancing this type of study. Our approach is based on a semiempirical TB model which includes fairly well all the important features of the band structures of the composing materials, and then uses a powerful renormalization technique to determine both the band structure and the corresponding wavefunctions which occur in the microstructures.

We have begun our analysis by considering a simple analytical continuum model, which reveals the peculiar occurrence and structure of interface states, caused by the coupling of effective masses with different signs. Then, we have introduced our microscopic approach, where the large rank of the TB Hamiltonian matrix is reduced systematically by a renormalization procedure. Applications to quantum wells and superlattices demonstrate a qualitative consistency with some features of the analytical model, but produce significantly more accurate results. In particular, the square magnitude of the different components of the interface wavefunctions on the various atomic orbitals of the basis set reveal the $s-p$ hybridization associated with the mixing between $\Gamma_6$- and $\Gamma_8$-derived bands. The simple analytical continuum model is still useful in interpreting some basic features of such states, but is unable to account quantitatively for the $\Gamma_6$-coupling, and even qualitatively for the $s-p$ mixing.

The microscopic calculations are based on a TB Hamiltonian, with parameters optimized as to reproduce reliably the overall band dispersion in the Brillouin zones of the composing materials, while retaining the needed accuracy for the effective mass tensors near the zone centers. The then renormalization-decimation procedure requires inversion only of small matrices of fixed rank, which becomes crucial for large supercells, since the computation scales only logarithmically with the supercell dimension. The weight of the wavefunction components on all the atomic sites and orbitals in the basis are accurately determined as residues at the poles of the corresponding Green's function matrix elements. Even the

wavefunction *amplitude* can be determined accurately by an alternative modified (two- or $n$-step) Lanczos method. The knowledge of accurate wavefunction amplitudes is clearly essential for further studies of both direct optical transitions and indirect transitions assisted by interface phonons.

A complete account of our methods of calculation and of our results is provided in a Ph.D. thesis,[1] and in an article in Phys. Rev. B.[2] Our results confirm, for example, that $(HgTe)_m$ $(CdTe)_8$ is a semiconductor for $m \lesssim 20$, a semimetal for $20 \lesssim m \lesssim 28$, and an inverted-gap semiconductor for $m \gtrsim 28$. Such behavior is a consequence of the peculiar inverted band structure of HgTe. The interesting relationship with the semimetallic $\rightarrow$ semiconductor transition which occurs in $Hg_{1-x}Cd_xTe$ alloys is also confirmed and quantitatively explained.

The issue of the valence band offset (VBO), which bears on several experimental effects and theoretical questions, has been previously investigated. Some debate still remains, but a large value for the VBO is generally accepted. We have performed our calculations for different VBO values, ranging from 0.0 to $-0.450\,eV$, and examined the corresponding confining effect on the various types of bands.

In quantum wells, the heavy-hole states, once confined, hardly change with increasing VBO, as expected. On the other hand, the interface states considerably descend in energy with increasing VBO. Such decrease is essentially linear in the VBO, and can be associated with the descent of the asymptotic energy of the interface states at the heterojunction, which is proportional to the VBO in the analytical model.

In superlattices, the effect of the VBO on the interface states is analogous to that in quantum wells. A smaller (larger) VBO implies a larger (smaller) HgTe well-width $L$ required to attain the semiconductor $\rightarrow$ semimetal transition. In $(HgTe)_m$ $(CdTe)_8$, for VBO$= -0.040\,eV$ we obtain $L \simeq 30\frac{a}{2}$, i.e., $m = 30$, whereas for VBO$= -0.450\,eV$ we obtain $L \simeq 20\frac{a}{2}$. By comparing with experimental data, this may be used as a criterion to further investigate the small vs. large VBO issue in these heterostructures.

## III. SUMMARY OF THE MOST IMPORTANT RESULTS FOR THE ELECTRICAL RESPONSE OF COMPOSITE SYSTEMS

A composite system (with the cermet topology) consists of inclusions of different electrical properties embedded in a continuous medium. There is great interest in a full theoretical understanding and computation of the electrical and transport properties of composite materials, which would allow the design of composites with required effective electrical and transport properties, such as conductivity, dielectric constant, absorption, and other optical characteristics. Extended applications include, for example, electrorheological fluids, and electron energy loss in random systems.

The theoretical problem consists of two parts: firstly, to find the response of an isolated inclusion, and secondly, to treat the interactions among the inclusions. The early and still basic results in this field are the Clausius-Mossotti (CM) relation, the Maxwell-Garnett (MG) formula, the Bruggeman symmetric and asymmetric formula, and the Debye result. All these results were obtained with the so-called macroscopic approach, which assumes that each inclusion in the system lies inside a cavity, surrounded by a medium characterized by the macroscopic effective dielectric constant. Only recently microscopic approaches have become available, which take into account the microscopic electric field produced by all the inclusions, interacting with one another. However, most microscopic approaches have still been limited to the dipole approximation. Such dipolar theories essentially lead to the CM relation. There have been some fully multipolar calculations, although mostly limited to simple systems, such as arrays of spheres or cylinders. These multipolar results largely deviate from the CM relation, when the inter-particle distance becomes comparable or less than one half of the particle diameter (corresponding to a volume fraction of 0.2). On one hand, these multipolar calculations correctly show the importance of higher multipoles. On the other hand, they seem to contradict many experimental results, which indicate that the CM relation still applies fairly well to much higher volume fractions.

We have developed a rigorous and systematic approach to solve this problem. Compared

with other methods in the literature, our theory has the following advantages: (1) all orders of multipoles moments are included; (2) the experimental slab configuration with surfaces is treated; (3) inclusions of arbitrary shapes and responses are considered; (4) arbitrary positions and distributions of the inclusions are treated.

The inclusion of all the multipole moments enables us to compute the exact response of composite systems. We have thus demonstrated, for example, that methods claimed to be exact in fact produce inaccurate results.[3] More importantly, we have demonstrated that in mean field theory, for system with isotropic two-particle distributions, the fields due to higher multipoles of the surrounding inclusions on any given particle precisely cancel. Hence, for isotropic pair distributions, the CM relation, the MG formula, and the Debye result still hold, even when all orders of multipoles are considered.[4,5] This has resolved the apparent discrepancy between the previous multipolar calculations for arrays and the experimental results for disordered systems.

The treatment of the slab configuration avoids the ambiguities and divergences of the long-range dipolar interactions, and is thus advantageous even for the study of bulk properties. More significantly, it allows to study thin-film systems, fully including surface effects. The presence of two surfaces, namely, the electrode plates, induces an infinite series of *image multipoles*, related to the actual multipoles. We have successfully applied this theory to the study electrorheological fluids, demonstrating the multipolar interactions between the suspended inclusions and the electrodes, as well as the precise interactions among all the inclusions. These results have shown that the widely used dipole or fixed-dipole approximations typically account for only a few percent of the exact multipolar interactions.[6–8] Furthermore, the ability to treat inclusion with arbitrary structure greatly broadens the range of applicability of our theory. For example, we have found that an electrorheological fluid consisting of metal spheres coated with a thin insulating layer exhibits electrostatic interactions enhanced by several order of magnitude.

We have also developed a theory of the nonlinear response of particles and composites. We have already obtained the exact their-order polarizability of a coated nonlinear sphere,

and shown that such particle structure can enhance the effective third-order susceptibility (Kerr coefficient) in a composite by several order of magnitudes.[9] Prior to that, it was widely believed that such exact solution for the third-order polarizability of coated spheres was impossible. The effect of the particle interactions is also crucial. We have shown that the multipolar interactions among the inclusions are controlled by the particle distribution. Even for isotropic pair distributions, there are significant nonlinear corrections to the CM relation.[10] More significantly, anisotropic pair distributions can modify the nonlinear resonance peak by more than one order of magnitude, while also changing the resonance frequencies.[9] This finding may have a considerable impact in the design of composite materials for optical-switching applications.

Quite recently, we have further developed our theory to treat exactly nonlinear composites with a power-law response.[11] Only two limiting results, namely, the weak (low field) and strong (high field) nonlinearities were known heretofore. We have now obtained the exact results for all strengths of the field. In fact, the ranges of the two previous limiting results are extremely narrow. Furthermore, for fields in between, we have found a remarkably complex and rich set of *multiple* solutions for the nonlinear response. This is quite unexpected and potentially significant, both theoretically and for experimental applications. The multiple solutions that we have found indicate that there are multiple metastable states in composite nonlinear materials. Each state corresponds to a different distribution of electric field. Some states generate a high capacity for storing energy, while other states correspond to low absorption or loss. The multiple solutions depend in a complex way on the response of the particles, the frequency of the exciting field, and the particle concentration and distribution. We still do not know how to switch the system from one state to another. But we feel that a complete understanding of these multiple solutions is likely lead to important applications in nonlinear optics.

## IV. LIST OF ALL PUBLICATIONS AND TECHNICAL REPORTS

The list of all the works that have been at least in part supported under this contract, with corresponding acknowledgements, coincides with the list of References at the end of this report.

Four Interim Progress Reports have been previously filed, covering the 1993-1996 periods of the contract.

## V. LIST OF ALL PARTICIPATING SCIENTIFIC PERSONNEL SHOWING ANY ADVANCED DEGREES EARNED BY THEM WHILE EMPLOYED ON THE PROJECT

Lorenzo Resca, Giuseppe Pastori Parravicini, Liang Fu, Marco Fornari, Hung-Hsin Chen (doctoral degree).

## VI. REPORT OF INVENTIONS

None.

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